

REMARKS

Claims 1-10 are pending and Claims 1-10 stand rejected. Claims 1,2, and 4-9 have been amended. New Claims 11 and 12 have been added. No new matter has been added to the application. Support for the amendments may be found throughout the application, but in particular on page 3, lines 21-26, page 5, line 25, and page 11, line 18.

The Examiner has refused to enter the substitute specification because a marked-up copy of the specification was not submitted. Additionally, the Examiner has requested a statement that no new matter has been added to the specification. It is requested that the amendments made to the specification in the Response dated July 29, 2002 be entered into the application. Attached to this Preliminary Amendment is a copy of the marked-up specification that the Examiner requested in the Office Action dated September 25, 2002 pursuant to 37 CFR 1.125(b). Additionally, it is stated that no new matter has been added to the specification by these amendments. In light of this statement and the attached substitute specification, it is requested that the previous amendments be entered and that the objection be withdrawn.

The Examiner also maintained the previously cited objections to the specification. It is requested that these objections be withdrawn for the reasons stated above.

Claim 2 has been rejected under 35 U.S.C. 112, second paragraph, as indefinite. In particular, the Examiner has taken the position that Claim 2 is not commensurate with the limitations of Claim 1. It is submitted that the amendments made to the claims

above are sufficient to overcome the rejection. Therefore, it is requested that the rejection be withdrawn.

Claims 5-10 have been rejected under 35 U.S.C. 112, second paragraph, as indefinite. Claim 5 has been rejected because Claim 5 is unclear to the Examiner. The Examiner has expressed confusion as to whether Claim 5 is a dependent claim or an independent claim. Therefore, Claim 5 has been amended to further clarify the meaning of Claim 5.

It is submitted that this amendment further clarifies that Claim 5 is an independent claim. It is requested that the rejection be withdrawn in light of the above amendment.

Claim 6 has been rejected as indefinite by the Examiner because the Examiner is confused as to how the additives (1)-(3) are "controlled" by an amount of the added elements. It is submitted that the "controlled" limitation of Claim 6 is a statement that the effects of the additives are controlled by the amounts of the elements present in the compound. The Examiner has also noted that the compositions of the added elements are not defined in Claim 6.

Claim 6 has been amended to clarify the issues raised by the Examiner. Therefore, it is requested that the rejection be withdrawn in light of the amendments presented above.

Claim 7 has been rejected as indefinite because the term "the ferromagnetic transition temperature" lacks sufficient antecedent basis in the claims. Claim 7 has also been rejected as indefinite because the Examiner is unsure as to what is meant by the

term "at least one of said amount of said combination. Claim 7 has been amended in order to address these issues. It is submitted that the rejection of Claim 7 has been rendered moot by the amendments made above. Therefore, it is requested that the rejection of Claim 7 be withdrawn.

Claims 8-10 have been rejected as indefinite as well. The Examiner has taken the position that these claims are not properly dependent upon Claim 6. Further, the Examiner has advanced that Claims 8-10 do not properly limit Claim 6. It is submitted that the Examiner is mistaken. Claims 8-10 limit the choice of additives available in Claim 6. Claim 6 permits the user to select one of three options (groups (1)-(3)). It is submitted that Claims 8-10 only permit the selection of group (2), thereby limiting Claim 6. Additionally, Claims 8-10 further limit Claim 6 by requiring the mixing of the additive to be done through the crystal-mixing process. Therefore, it is submitted that the rejection is improper for this reason. It is requested that the rejection be withdrawn.

The Examiner has also rejected Claims 8-10 because they contain the term "the ferromagnetic state." The Examiner has noted that no antecedent basis exists for this term in Claim 6. Claims 8-9 have been amended to address this issue. It is submitted that no amendment is needed for Claim 10 as Claim 10 does not contain the rejected language. Therefore, in light of the above arguments and positions, it is requested that the rejection be withdrawn.

Claims 6-7 have been rejected under 35 U.S.C. 112, first paragraph, as containing subject matter that is not adequately described in the specification. The Examiner has taken the position that Claims 6 and 7 are not supported by the

specification because there is allegedly no teaching of controlling the additives of (1)-(3) by adding an amount of the added elements, Ti, Mn, Cu, n-type dopant, p-type dopant, and combinations of the added elements. The Examiner has taken the position that the specification teaches that the ferromagnetic properties of the compounds are controlled by the amount and composition of the additives of (1)-(3). It is submitted that the above amendments made to the claims address this issue as well and it is requested that the rejection be withdrawn in light of the clarifications made to the claims.

Claims 1, 4, and 5 remain rejected under 35 U.S.C. 102(e) as anticipated by the Stoner patent. It was previously argued that the Stoner reference could not anticipate the claimed invention because the Stoner reference did not disclose (or suggest) ferromagnetic properties. The Examiner, however, has not found this argument persuasive. She has taken the position that the Stoner reference clearly teaches the claimed compound and that it, therefore, must inherently possess the claimed ferromagnetic properties.

It is submitted that the present invention is characterized by its being a ferromagnetic ZnO-type compound film with a single-crystalline structure. The ferromagnetic characteristics are obtained by crystal-mixing the transition elements (which includes Fe) in ZnO of a single crystal structure. It is submitted that unless the compound is not of single-crystalline structure or unless the transition metal element (or the like) is not crystal-mixed, the film does not exhibit the ferromagnetic properties. In the present invention, these added elements are limited to at least two kinds, or at least one kind of these elements and an n-dopant or p-dopant. By adding elements of

different kinds, the present invention possesses easily adjusted ferromagnetic properties.

It is also submitted that Stoner discloses a semiconductor device such as a SAW device that uses $\text{Zn}_{1-x}\text{Y}_x\text{O}$. Stoner also discloses the addition of transition elements to the composition. However, it is noted that Stoner only adds one kind of element, Y, to the ZnO and does not disclose (or suggest) that two or more elements may be added to provide the presently claimed ferromagnetic properties. Therefore, it is submitted that the reference does not teach all of the claimed limitations and is insufficient to anticipate the present invention. It is requested that the rejection be withdrawn.

Claims 1, 4, and 5 remain rejected under 35 U.S.C. 102(b) as anticipated by the Nitta patent. The Examiner has taken the same position regarding the teachings of the Nitta patent as she has with the Stoner patent (see preceding discussion).

It is submitted that this rejection is not well taken either. It is noted that Nitta discloses a method for manufacturing a sulfide ceramic body, and for the starting oxide material, ZnFeO and NiZnO are indicated. However, it is submitted that it is clear from the reference that the body is a lump of particles having sulfide layers and that it is not a film. Therefore, the Nitta composition cannot possess a single-crystalline structure, as the presently claimed invention does. Further, it is submitted that these deficiencies results in the Nitta composition being unable to exhibit ferromagnetic properties. Finally, it is noted that Nitta only discloses the use of one kind of element. Therefore, for the reasons presented above and for the reasons set forth in the traversal of the rejection in view of the Stoner reference, it is submitted that this rejection is also

improper because the Nitta reference does not teach all of the claimed limitations of the present invention. Thus, it is requested that the rejection be withdrawn.

Claims 1, 4, and 5 remain rejected under 35 U.S.C. 102(b) as anticipated by the Hager patent. As with the Stoner and Nitta patents, the Examiner has advanced the same inherency argument described above as the support for the rejection of these claims in light of the Hager patent.

It is submitted that the rejection is not well taken. The previous discussion of the Nitta and Stoner patents are relied upon in the traversal of this rejection. It is submitted that while Hager discloses a ZnO film that has been doped with Rh or Ru, Hager does not discuss (or suggest) that two or more metal elements are (or can be) crystal-mixed. Therefore, it is submitted that the combination of the references fails to teach all of the claimed limitations of the invention. Further, it is submitted that there is no motivation to combine these references to create the claimed invention, especially because the references fail to teach all of the limitations of the present invention. Thus, it is requested that the rejection be withdrawn for these reasons.

Claims 1, 4, and 5 have been rejected under 35 U.S.C. 102(b) as anticipated by the Dausch patent. Again, the Examiner has advanced the inherency argument set forth in the discussion of the rejection based upon the Stoner patent.

It is submitted that this rejection is not well taken because Dausch discloses a metal oxide-doped ZnO pigment. It is submitted, though, that it is clear from the reference that the pigment is manufactured by mixing and sintering (for example, ZnO and MnC) and that it is not a single-crystalline film. Therefore, the Dausch composition

cannot possess a single-crystalline structure. Additionally, the Dausch composition cannot possess ferromagnetic properties for the reasons disclosed above. Therefore, it is requested that the rejection be withdrawn as the Dausch reference fails to disclose all of the limitations of the present invention.

Claims 1 and 3-5 remain rejected under 35 U.S.C. 102(b) as anticipated by the Miyazaki reference. The Examiner has taken the position that the Miyazaki reference teaches a ZnO doped with 1-10 at% of at least one of Cr, B, and Ga, as well as the method for producing these compounds. The Examiner has also noted that B and Ga are known to be n-type dopants. The Examiner has also advanced that the claimed ferromagnetic properties of the claimed compounds would be inherently possessed by the compounds of the Miyazaki patent. Therefore, the Examiner has not found Applicants' previous arguments persuasive and has maintained the rejection.

It is submitted that this rejection is not well taken. Miyazaki discloses a low emissivity film with oxide films, metal films, etc. that have been laminated on a substrate. Miyazaki also discloses at least one of a ZnO layer that contains at least one of Si, Ti, Cr, B, Mg, Sn, and Ga doped on a metal layer farthest from the substrate. However, it is submitted that the substrate 1 is made of glass or plastic (see lines 52-53 of Col. 4) and that the metal layer (3) that is below the doped ZnO layer (4) is made of either Ag, Au, Cu, or Pd (see lines 4-8 of Col. 6). It is submitted that the ZnO layer cannot, then, be a single-crystalline structure. This is because a single-crystalline structure ZnO layer requires that the substrate upon which it is deposited have a single-crystalline structure as well. Therefore, it is submitted that the rejection is improper for

this reason. Additionally, it is noted that the Miyazaki reference fails to teach all of the claimed limitations as Miyazaki does not disclose or suggest ferromagnetic properties. Thus, it is requested that this rejection be withdrawn for the above reasons.

Claims 1, 2, 4, and 5 have been rejected under 35 U.S.C. 102(b) as anticipated by the Pfrommer reference. The Examiner has taken the position that because the composition of the claimed compounds and those disclosed in the Pfrommer reference overlap, the Pfrommer compounds must be ferromagnetic as well.

It is submitted that the rejection is not well taken. Pfrommer discloses ZnO with metal oxide-doped colorants and UV absorbers. Additionally, the Pfrommer compositions are disclosed as being usable in cosmetics. However, this use prevents the compositions from being a film or from possessing a single-crystalline structure. Therefore, it is requested that the rejection be withdrawn because the reference fails to teach all of the claimed limitations.

In the event this paper is not timely filed, Applicants hereby petition for an appropriate extension of time. The fee for this extension may be charged to our Deposit

Account No. 01-2300, referring to client-matter number 107400-00016, along with any other fees which may be required with respect to this application.

Respectfully submitted,

A handwritten signature in dark ink, appearing to read 'D. Daniel Dzara, II', is written over a horizontal line.

D. Daniel Dzara, II
Registration No. 47,543

Customer No. 004372
ARENT FOX KINTNER PLOTKIN & KAHN, PLLC
1050 Connecticut Avenue, N.W.,
Suite 400
Washington, D.C. 20036-5339
Tel: (202) 857-6000
Fax: (202) 638-4810

Enclosure: Marked Up Copy of the Claims
 Marked-Up Copy of the Specification
 Request for Continued Examination

MARKED UP COPY OF CLAIMS

1. (Amended) A ferromagnetic ZnO-type compound film having a single-crystalline structure, wherein a ZnO-type compound contains at least two metals selected from [a] the group consisting of V, Cr, Fe, Co, Ni, Rh, Ru, Ti, Mn, and Cu by being crystal-mixed.

2. (Amended) The ferromagnetic ZnO-type compound film of claim 1, wherein said ZnO-type compound contains at least two types of metals selected from [a] the group consisting of [said transition metallic elements] V, Cr, Fe, Co, Ni, Rh and Ru, and the group consisting of Ti, Mn, and Cu, wherein at least one metal is selected from each group.

4. (Twice Amended) A ferromagnetic ZnO-type compound film having a single-crystalline structure, wherein a ZnO-type compound is added with at least one of
(1) at least [one] two metallic [element] elements selected from a group consisting of [transition metallic elements of] V, Cr, Fe, Co, Ni, Rh, [or] Ru, Ti, Mn, and Cu, and
(2) at least [two] one metallic [elements] element selected from a group consisting of [said transition metallic elements] V, Cr, Fe, Co, Ni, Rh, Ru, Ti, Mn and Cu, and
[(3) either one of said (1) or (2), and] at least one of an n-type dopant, and a p-type dopant

in an amount such that said ferromagnetic ZnO-type compound has a specific ferromagnetic transition temperature.

5. (Twice Amended) A ferromagnetic ZnO-type compound film having a single-crystalline structure, wherein a ZnO-type compound is added with at least one of

(1) at least two metallic elements selected from a group consisting of V, Cr, Fe, Co, Ni, Rh, Ru, Ti, Mn, and Cu, and

(2) at least one metallic element selected from a group consisting of V, Cr, Fe, Co, Ni, Rh, Ru, Ti, Mn, and Cu, and at least one of an n-type dopant and a p-type dopant in an amount such that [in which any one of (1) to (3) of claim 4 is added so that] said ferromagnetic ZnO-type compound has a specific light-filtering characteristic.

6. (twice amended) A method for adjusting ferromagnetic characteristics of a ferromagnetic ZnO-type compound, wherein said method comprises controlling the amount of one of (1) to (3) added to the ZnO-type compound, wherein (1) to (3) are:

(1) at least one metallic element selected from a group consisting of transition metallic elements [of] V, Cr, Fe, Co, Ni, Rh or Ru,

(2) at least two metallic elements, one selected from a group consisting of said transition metallic elements, and the other selected from the group consisting of Ti, Mn and Cu, and

(3) either one of said (1), or (2), and at least one of an n-type dopant, and a p-type dopant

[is added to said ZnO-type compound for adjusting ferromagnetic characteristics, said one of (1) to (3) being controlled by an amount of added elements, Ti, Mn, Cu or n-type dopant or p-type dopant or by a combination of said added elements].

7. (twice amended) The [adjusting] method of claim 6, wherein the ferromagnetic characteristic is a ferromagnetic transition temperature, and [the ferromagnetic transition temperature is adjusted to a desired temperature by controlling] wherein the

amount of said one of (1) to (3) added to the ZnO-type compound is controlled so as to produce a predetermined ferromagnetic transition temperature [at least one of said amount of said combination].

8. (Twice Amended) The [adjusting] method of claim 6, wherein the [ferromagnetic state] ZnO-type compound is stabilized by crystal-mixing said at least two [types of] metallic elements [as listed in said] (2), so that [the] there is an entire energy [decreases] decrease by kinetic energy based on holes or electrons introduced by said crystal-mixing metallic elements themselves.

9. (Twice Amended) The adjusting method of claim 6, wherein the [ferromagnetic state] ZnO-type compound is stabilized by crystal-mixing said at least two [types of] metallic elements [as listed in said] (2), so that a magnetic interaction between metallic atoms is controlled by holes or electrons introduced by said crystal-mixing metallic elements themselves.



FERROMAGNETIC ZnO-TYPE COMPOUND INCLUDING TRANSITION
METALLIC ELEMENT AND METHOD FOR ADJUSTING FERROMAGNETIC
CHARACTERISTICS THEREOF

5

FIELD OF THE INVENTION

The present invention relates to a
single-crystalline ferromagnetic ZnO-type compound
realizing ferromagnetic characteristics by
crystal-mixing at least one of transition elements such
10 as V, Cr, Fe, Co, Ni, Rh or Ru to a light-transmitting
ZnO-type compound and a method for adjusting ferromagnetic
characteristics thereof. More particularly, it relates
to a ferromagnetic ZnO-type compound exhibiting desired
ferromagnetic characteristics, such as ferromagnetic
15 transition temperature, and a method for adjusting the
ferromagnetic characteristics thereof.

BACKGROUND OF THE INVENTION

20 If it is possible to obtain single-crystalline
ferromagnetic thin films exhibiting high ferromagnetic
characteristics while transmitting light, it will be
possible to provide light isolators or to perform
high-density magnetic memory as it is required in
transmitting a large amount of information and thus to
25 manufacture electronic materials required for
transmission of large amount of information in the future.
It is therefore being wanted for materials exhibiting

ferromagnetic characteristics while transmitting light.

On the other hand, ZnO-type compounds are advantaged through their characteristics of exhibiting a large band gap of 3.3 eV and transmitting light of wavelengths ranging
5 from blue to ultraviolet, and due to their large binding energy of their excitons when compared to, for instance, GaN, remarkable progresses are being expected in the field of manufacturing optical devices such as light quantum computers employing coherent spin states once it is
10 possible to exhibit ferromagnetism through these materials. However, while there are conventionally known cases in which ZnO is doped using Mn, ZnO will be in an antiferromagnetic state and no cases have so far been reported in which ZnO-type compounds are in ferromagnetic
15 conditions.

As noted, if it would be possible exhibit ferromagnetic characteristics by using ZnO-type compounds, quite a large variety of applications to devices utilizing magnetic-optical effects will be provided in which these
20 compounds are used in combination with light-emitting elements such as semiconductor laser of ZnO-type compounds exhibiting large binding energy of excitons or in which light reflecting magnetic states are generated.

In case of arranging memories of ferromagnetic bodies
25 by irradiating such light and varying magnetic states, it will be necessary to set ferromagnetic characteristics to be desired ones in which, for instance, a ferromagnetic

transition temperature (Curie temperature) is set to be a temperature that is varied upon radiation of light (a temperature slightly higher than room temperature).

5 SUMMARY OF THE INVENTION

The invention has been made in view of these circumstances, and it is an object thereof to provide a ferromagnetic ZnO-type compound exhibiting ferromagnetic characteristics by using a light-transmitting ZnO-type
10 compound.

It is another object of the present invention to provide a method for adjusting ferromagnetic characteristics of the ferromagnetic ZnO-type compound in obtaining the ferromagnetic ZnO-type compound which
15 ferromagnetic characteristics such as ferromagnetic transition temperatures may be adjusted.

The inventors of the present invention have found upon performing various studies for obtaining a single-crystalline structure with ferromagnetic
20 characteristics by using a ZnO-type compound that is a particularly suitable material transmitting light, that the ion radii of transition elements such as Ti, V, Cr, Mn, Fe, Co or Ni approximate to that of Zn and that single-crystalline structures may be sufficiently
25 obtained even by substituting (crystal-mixing) more than 50% of Zn, that even though only antiferromagnetic characteristics may be obtained by crystal-mixing Mn to

ZnO, ferromagnetic characteristics may be obtained adding holes or electrons (increasing or decreasing electrons) to the electron condition of Mn in this state (with 5 d-electrons), that similar effects as by adding holes to Mn may be achieved by crystal-mixing Cr or V, which number of d-electrons are less than those of Mn, to the ZnO-type compound, and that similar effects as by doping electrons to Mn may be achieved by crystal-mixing Fe, Co or Ni to the ZnO-type compound, and finally came to find out that by crystal-mixing at least one of transition elements such as V, Cr, Fe, Co, Ni, Rh or Ru to the ZnO-type compound, a stable ferromagnetic condition may be achieved by simply crystal-mixing these metallic elements.

By further continuing these studies, the inventors have found that transition elements such as Ti, V, Cr, Mn, Fe, Co or Ni assume high spin states with electron spins s of $5/2$, $4/2$, $3/2$, $2/2$ or $1/2$, that ferromagnetic transition [temperatures are] temperature is variable by varying their [densities, performing] densities (concentration of added element(s) or amount of added element(s)), crystal-mixing by varying combinations or ratios of two [more than two] or more types thereof or by adding n-type and/or p-type dopants, that the ferromagnetic state may be stabilized than compared to antiferromagnetic or paramagnetic states, that an energy in the ferromagnetic state (for instance, an energy with which the ferromagnetic state may be maintained in an ordinary condition though

an antiferromagnetic state is assumed in the presence of slightest differences) is adjustable, and that desired filtering functions may be exhibited by selectively performing crystal-mixing of [more than two]two or more types of the above transition [matallic]metallic elements that exhibit different minimum transmission wavelengths, and finally came to find out that by adjusting densities or mixing ratios of these transition metallic elements, a single-crystalline and ferromagnetic ZnO-type compound exhibiting desired magnetic characteristics may be obtained.

The ferromagnetic ZnO-type compound according to the present invention is a ZnO-type compound containing at least one metal selected from a group of transition metallic elements consisting of V, Cr, Fe, Co, Ni, Rh and Ru.

It should be noted that the term "ZnO-type compound" here denotes an oxide including Zn, a concrete example of which is ZnO, respective oxides of a IIA group element with Zn, a IIB group element with Zn or IIA group element and IIB group element with Zn.

With this structure, with the above-listed transition metallic elements which iron radii approximate to those of II group elements such as Zn, single-crystalline structures of Wurtzite structure may be maintained even upon substituting not less than 50 at% of Zn, and will exhibit ferromagnetic characteristics with increased holes or electrons than compared to Mn while maintaining its

transparency.

By containing at least two types of metals selected from a group consisting of the above metals, Ti, Mn and Cu, conditions of d-electrons of the metallic elements
5 will be respectively different so that ferromagnetic characteristics will be varied in a more direct manner than achieved by doping holes or electrons so that ferromagnetic characteristics such as ferromagnetic transition temperatures may be adjusted.

10 By performing doping by using at least [either] one of an n-type dopant [or] and a p-type dopant, the dopant will enter a matrix of ZnO so that it will act on d-electrons close to the matrix of ZnO, though their effects will not be so much direct as it is the case with transition element,
15 and holes or electrons are varied to enable adjustments of ferromagnetic characteristics.

According to the method for adjusting ferromagnetic characteristics of a ZnO-type compound, [at least] one of
(1) to (3),

20 (1) at least one metallic element selected from a group consisting of transition metallic elements of V, Cr, Fe, Co, Ni, Rh and Ru,

(2) at least two metallic elements selected from a group consisting of the above transition metallic elements, Ti,
25 Mn and Cu, and

(3) either (1) or (2) and at least one of [the above (1), (2),] an n-type dopant, and a p-type dopant

is added to the ZnO-type compound for adjusting ferromagnetic characteristics by adjusting [densities] an amount of added element (s) of the above transition elements, Ti, Mn, Cu or n-type dopant or p-type dopant or by [varying combinations] a combination of the added element (s). [of these metallic elements.]

Particularly, it is possible to adjust the ferromagnetic transition temperature to be a desired temperature by using at least one method of adjusting the density (the density of transition elements, metallic elements such as Mn and dopants), and varying combinations of metallic elements as listed in above (2); to stabilize the ferromagnetic state by adjusting the ferromagnetic energy by crystal-mixing at least two types of metallic elements as listed in above [(2) and by decreasing] (2), so that the entire energy [through] decreases by kinetic energy based on holes or electrons introduced by said crystal-mixing [by holes or electrons introduced by the] metallic elements themselves; and to further stabilize the ferromagnetic state by crystal-mixing at least two types of metallic elements as listed in above [(2) and by controlling the size and sign of] (2), so that a magnetic interaction between metallic atoms [through] is controlled holes or electrons introduced by the metallic elements themselves.

[It is further possible to obtain a ferromagnetic ZnO-type compound with desired light-filtering

characteristics by crystal-mixing at least two types of metallic elements as listed in above (2), by controlling the size and sign of magnetic interaction between metallic atoms through holes or electrons introduced by the metallic elements themselves and by controlling transmitting characteristics of light owing to crystal-mixing of metallic elements.]

It is further possible to obtain a ferromagnetic ZnO-type compound with desired light-filtering characteristics by crystal-mixing at least two types of metallic elements as listed in above (2), so that transmitting characteristics of light is controlled by holes or electrons introduced by said crystal-mixing metallic elements themselves.

15

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is an explanatory view showing one example of a apparatus for forming a ferromagnetic ZnO-type compound thin film according to the present invention;

20 Fig. 2 is a diagram illustrating differences ΔE between entire energy of antiferromagnetic body and entire energy of ferromagnetic body when a transition element such as V, Cr is crystal-mixed to ZnO;

Figs. 3(a) and 3(b) are diagrams illustrating variations in ferromagnetic transition temperatures and magnetic moments upon variations in density of transition element that is crystal-mixed to ZnO;

25

Figs. 4(a) and 4(b) are diagrams illustrating variations in ferromagnetic transition temperatures depending on ratios of crystal-mixing more than two types of transition elements; and

5 Fig. 5 is an explanatory view showing variations in magnetic states when an n-type or p-type dopant is added to, for instance, Mn.

DETAILED DESCRIPTION

10 The ferromagnetic ZnO-type compound and the method for adjusting its ferromagnetic characteristics according to the present invention will now be explained with reference to the drawings. The ferromagnetic ZnO-type compound according to the present invention is a ZnO-type
15 compound containing at least one metal selected from a group consisting of transition metallic elements of V, Cr, Fe, Co, Ni, Rh and Ru.

As already described, the inventors of the present invention have found out through various studies for
20 obtaining a ferromagnetic material using a ZnO-type compound that in case of transition [elementlic] metallic elements V, Cr, Fe, Co, Ni, Rh and Ru, these transition [elementlic] metallic elements exhibit ferromagnetism by performing crystal-mixing of only these elements in a
25 single manner due to the fact that 3d-electrons are increased/decreased through Mn, which itself is antiferromagnetic, as indicated by the difference ΔE

between antiferromagnetic entire energy and ferromagnetic entire energy as illustrated in Fig. 2. While the ratio of mixed crystal to Zn in ZnO is 25 at% in this example, ferromagnetism can also be achieved already with a mixed
5 crystal ratio of several %, causing no damages on crystallinity and transparency though this ratio be increased, and satisfactory ferromagnetism can be achieved with a ratio of 1 at% to 99 at%, preferably 10 at% to 80 at%. The transition metallic element may be used singly
10 or, as it will be described later, by mixed crystal (alloying) more than two types thereof.

For forming a thin film using such a ZnO-type compound containing a transition metallic element, a substrate 5 that is made, for instance, of sapphire for growing a
15 ZnO-type compound is disposed on a substrate holder 4 within a chamber 1 capable of maintaining an ultrahigh vacuum condition of approximately 1.33×10^{-6} Pa, wherein the substrate 5 may be heated through a heater 7 as illustrated in a schematic explanatory view of a MBE apparatus of Fig.
20 1. A cell 2a containing therein an elemental material (source) Zn comprising the compound to grow, a cell 2b containing therein a transition [elementlic] metallic element such as Fe (though only one cell is illustrated, [more than] two or more cells are provided when
25 crystal-mixing [more than] two or more types of metals), a cell 2c containing therein an n-type dopant such as Ga, Al or In, and RF radical cells 3a, 3b for generating radical

oxygen O and radical nitrogen N are disposed to oppose the substrate 5 held by the substrate holder 4. It should be noted that solid materials such as Zn or transition metallic elements might assume atomic states by putting
5 oxides of these metals into the cells.

Though not illustrated, the cells 2a to 2c into which the solid bodies (elements) are put are respectively provided with heaters such that solid body sources are put into atomic states for evaporation through heating,
10 and the radical cells 3a, 3b are activated by RF (radio frequency) coils 8 as shown in the drawing. As for the Zn, transition metallic elements and n-type dopant materials, a solid body source of a purity of 99.99999% is put into an atomic state while an atomic gas of 99.99999%
15 in which O₂ is activated through the RF radical cells is used as O, and N⁺ or N₂ in an excited state is used by activating N₂ molecules or N₂O in the radical cells. It should be noted that Ga or transition metallic elements might also be put in an atomic state by irradiating electromagnetic waves
20 of microwave regions to molecular gas.

While making ZnO grow, Ga serving as an n-type dopant, an atomic N as a p-type dopant, and an atomic transition [elementlic] metallic element such as Fe are simultaneously poured onto the substrate 5 at a flow rate of 1.33×10^{-5}
25 Pa, a flow rate of 6.65×10^{-5} Pa, and a flow rate of 1.33×10^{-5} Pa, respectively, for growing at a temperature of 350 to 750°C in order to grow a ZnO thin film 6 crystal-mixed

with a transition metallic element. While doping is exemplarily performed using an n-type dopant or a p-type dopant in the above explanations, no dopants are used for the doping but doping is only performed using transition
5 elements including Mn, Ti and Cu in the examples as illustrated in Fig. 2 as well as Tables 1 and 2 as will be described later.

The ZnO thin film in which V, Cr, Fe, Co and Ni are crystal-mixed exhibits ferromagnetism as shown in Fig.
10 2 in which V, Cr, Fe, Co and Ni respectively exhibit a difference ΔE between antiferromagnetic energy and ferromagnetic energy of 20×13.6 meV, 15×13.6 meV, 10×13.6 meV, 14×13.6 meV and 18×13.6 meV. It should be noted that the data of Fig. 2 are data obtained through
15 first principle calculation in which simulation is performed using atomic numerals as input parameters.

While the ZnO compound is doped with a transition [elementlic] metallic element in this example, similar structures as ZnO may be obtained also with ZnO-type
20 compounds in which a part of Zn of ZnO is substituted by other II-group elements such as Mg or Cd, and it is similarly possible to obtain a ferromagnetic single-crystalline structure.

According to the ferromagnetic ZnO-type compound of
25 the present invention, a transition metallic element having ion radius that are substantially identical to that of Zn are crystal-mixed such that Zn^{2+} is substituted by Fe^{2+}

or similar of the transition metallic element for maintaining the Wurtzite structure. Moreover, since the above transition metallic elements such as Fe assume electron structures in which d-electrons are increased
5 than compared to Mn, the ferromagnetic state is stabilized as it is as illustrated in Fig. 2. Further, as illustrated in Tables 1 and 2 as will be described later, this ferromagnetic ZnO exhibits a large magnetic moment so that a Fe-containing ZnO-type compound having a larger magnetic
10 moment $4.04 \times 9.274 \text{ J/T}$ ($4.04 \mu_B$ (Bohr magneton)) than that of a Fe element (magnetic moment $2 \times 9.274 \text{ J/T}$ ($2 \mu_B$)), and it is possible to obtain a ferromagnetic magnet with extremely strong magnetism.

Variations in magnetic characteristics have then
15 been tested by varying densities of transition metallic elements. In addition to the above examples in which transition [elementlic] metallic metals of a density of 25 at% are contained, those of a density of 50 at% were manufactured for testing respective magnetic moments (\times
20 9.274 J/T) and ferromagnetic transition temperatures (degree K). The magnetic moments and ferromagnetic transition temperatures have been obtained by measuring magnetizing rates using a SQUID (super conducting quantum interference device). The results are shown in Tables 1
25 and 2. It is obvious from Tables 1 and 2 that the ferromagnetic transition temperature tends to rise the higher the crystal-mixing ratio becomes (the higher the

density becomes) and increases substantially proportional to the crystal-mixing ratio. This relationship is shown in Fig. 3. It can further be understood that the ferromagnetic interaction between spins is also increased
5 in accordance with increased in densities of transition elementlic elements and that the magnetic moments increase.

|

Table 1: Magnetic characteristics with transition elements
of 25 at%

Type of transition element	Density of transition element (at%)	Magnetic moment (μ_B)	Ferromagnetic transition temperature (degree K)
V	25	2.42	451
Cr	25	3.80	600
Fe	25	4.04	786
Co	25	2.96	528
Ni	25	1.88	389

Table 2: Magnetic characteristics with transition elements
of 50 at%

Type of transition element	Density of transition element (at%)	Magnetic moment (μ_B)	Ferromagnetic transition temperature (degree K)
V	50	2.58	681
Cr	50	3.95	792
Fe	50	4.02	959
Co	50	2.97	765
Ni	50	1.89	698

As already described, the transition metallic elements will assume high spin states with electron spins of $5/2$, $4/2$, $3/2$, $2/2$, $1/2$, and as it is further evident from the Tables 1 and 2 as well as Figs. 3(a) and 3(b), it is possible to adjust and control the ferromagnetic interaction between spins and the ferromagnetic temperatures by varying the densities. It should be noted that it is preferable in view of practical use that the ferromagnetic transition temperature be not less than 150 degree K.

The inventors of the present invention have further found out that it is possible to adjust conditions of holes or electrons and to concurrently exhibit respective magnetic characteristics by crystal-mixing [more than] two or more types of transition metallic elements. For example, Fe and Mn were crystal-mixed to be 25 at% as a whole and values x of $\text{Fe}_{0.25-x}\text{Mn}_x\text{Zn}_{0.75}\text{O}$ were respectively varied. It was consequently possible to largely vary the ferromagnetic transition temperature, to be 0 degree K when $x=0.15$ is satisfied, and to select a range for x between 0 to 0.15 for setting a desired ferromagnetic transition temperature as illustrated in Fig. 4(a). By similarly crystal-mixing Fe and Co to be 25 at% and respectively varying values x of $\text{Fe}_{0.25-x}\text{Co}_x\text{Zn}_{0.75}\text{O}$, ferromagnetic transition temperatures may be varied while maintaining a ferromagnetic state as illustrated in Fig. 4(b). Though not shown in the drawings, it is also possible to obtain magnetic moments in accordance with respective mixing ratios.

While ferromagnetic characteristics were varied by doping not less than two types of transition metallic elements in the above examples, the amount of holes or electrons may similarly be varied by doping an n-type dopant or a p-type dopant for varying the ferromagnetic states. In this case, the n-type or p-type dopant will enter a conduction band or a valence band of ZnO to act on adjoining d-electrons of transition metallic elements such that not

all of the doped dopants will act as a whole, the action on the d-electrons will also cause variations in ferromagnetic states and also vary ferromagnetic transition temperatures. Doping, for instance, an n-type
5 dopant also means supply of electrons so that doping an n-type dopant while crystal-mixing Fe will cause the same effects as adding Co further to Fe, and that doping a p-type dopant to Fe will cause the same effects as adding Mn to Fe.

10 A relationship of ΔE of Mn to a density of impurities (at%), in which Mn, which variations in ΔE obtained by subtracting ferromagnetic energy from antiferromagnetic energy according to doping the n-type or p-type dopant (electrons or holes) are remarkable, is crystal-mixed to
15 ZnO and is further doped with the impurities (holes or electrons) is illustrated in Fig. 5. By introducing holes at a ratio of not less than approximately 10%, the antiferromagnetic state will be converted to a ferromagnetic state, the ferromagnetic characteristics
20 will be varied in accordance with densities thereof, and to adjust the ferromagnetic characteristics thereof. Other transition metallic elements originally exhibit ferromagnetism so that no large differences exist between antiferromagnetism and ferromagnetism, but the
25 ferromagnetic states may be similarly varied and the ferromagnetic transition temperatures may be adjusted. It should be noted that unlike the above adjustments

performed by crystal-mixing not less than two types of transition metallic elements, magnetic moments themselves will maintain constant values adjustments depending on transition elements materials that are crystal-mixed to
5 ZnO in case of performing adjustments using dopants.

The n-type dopant may be B, Al, In, Ga, Zn or H, and raw materials for the doping may also be oxides of the above. The donor density is preferable not less than $1 \times 10^{18} \text{ cm}^{-3}$. In case doping is performed in a density of
10 approximately 10^{20} to 10^{21} cm^{-3} , it will correspond to a crystal-mixing ratio of approximately 1 to 10%. The p-type dopant may be atomic like N, as explained above, such as N^+ or N_2 in an excited state. While it is hard to perform doping using a p-type dopant, the p-type density may set
15 to be large by simultaneously doping a slight amount of n-dopant.

Upon performing further studies, the inventors have found out that minimum transmitted wavelengths differ depending on transition elementlic materials to be
20 crystal-mixed to ZnO, that the minimum wavelength of transmitted light is adjustable by mixing not less than two types of transition metallic elements to be crystal-mixed, and that light filter for cutting light having a wavelength that is not more than a desired one
25 may be formed. In other words, a ferromagnetic ZnO-type compound that transmits light of a desired wavelength may be obtained. The minimum wavelengths of light to be

transmitted when crystal-mixing 25 at% of the respective transition elementlic elements to ZnO are as illustrated in the Table 3 below.

Table 3: Minimum wavelengths of light to be transmitted
5 when crystal-mixing transition elements

Type of transition element	Density of transition element (at%)	Minimum wavelength (nm)
ZnO:V	25	375
ZnO:Cr	25	426
ZnO:Fe	25	412
ZnO:Co	25	415
ZnO:Ni	25	390
ZnO:Mn	25	485

In other words, according to this example, it is possible to obtain a ferromagnetic magnet that transparent to light of a desired wavelength.

10 As explained so far, the entire energy may be varied in the present invention owing to kinetic energy of holes or electrons introduced by metallic elements themselves that are crystal-mixed, and since the holes or electrons that are introduced are adjusted to decrease the entire
15 energy, the ferromagnetic state may be stabilized. The size and sign of magnetic interaction between metallic atoms are varied by introducing holes or electrons, and by controlling these through the holes and electrons, the ferromagnetic state may be stabilized.

20 While a MBE (molecular beam epitaxy) apparatus is used for performing the method of forming a thin film of

ZnO-type compound containing therein transition metallic elements in the above example, it is similarly possible to perform film forming by using a MOCVD (metal organic chemical vapor deposition) apparatus. In this case, 5 metallic materials such as Zn or transition element are introduced into the MOCVD apparatus in a form of an organic metallic compound such as dimethyl zinc. By using such MBE or MOCVD methods, it is possible to perform film forming in a non-equilibrium state and to dope transition metallic 10 elements at desired densities. The film forming methods for the thin films are not limited to the above methods, and it is alternatively possible to form thin films through a laser abrasion method in which Zn oxide solid bodies, transition metallic element metals or solid bodies of 15 oxides are used as targets and wherein film forming is performed while irradiating activated oxygen on the substrate.

In case of performing doping using transition metallic elements or oxides thereof as raw materials, it 20 is also possible to use ECR plasma in which atomic states are assumed through electron excitation using radio frequency waves, laser, X rays or electron beams. ECR plasma may also be employed when using an n-type or p-type dopant. Such ECR dopant is advantaged in that doping may 25 be performed in a atomic state up to a high density.

According to the present invention, a ferromagnetic single-crystalline structure may be obtained by simply

making the ZnO-type compound contain transition metallic elements, application to high-performance communication of information and quantum computers is enabled for use in quantum computers and large-capacity optical magnetic
5 memory and as optical electronics materials covering a scope ranging from visible-light to ultraviolet regions by combining these with ZnO that are already realized and used as n-type and p-type transparent electrodes, or with optical fibers.

10 Although preferred example have been described in some detail it is to be understood that certain changes can be made by those skilled in the art without departing from the spirit and scope of the invention as defined by the appended claims.

Abstract of the Disclosure

The ZnO-type compound contains at least one metal selected from a group of transition elements consisting of V, Cr, Fe, Co, Ni, Rh and Ru. Ferromagnetic characteristics are adjusted by adjusting densities of these transition elements, by varying combinations of [more than] two or more types of metals including Mn, or by adding dopants. It is consequently possible to obtain a ferromagnetic ZnO-type compound exhibiting ferromagnetic characteristics by using a light-transmitting ZnO-type compound, and to obtain a ferromagnetic ZnO-type compound exhibiting desired ferromagnetic characteristics.